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HIGH-SPEED OXIDIZING GASIFICATION OF BENZINE

By M. I. Demnet'yeva, M. A. Rivin,
and D. M. Rudkovskiy

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HIGH-SPEED OXIDIZING GASIFICATION OF BENZINE

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Following is the translation of an article by M. I. Demnet'yeva, M. A. Rivin, and D. M. Rudkovskiy, entitled "Vysokoskorostnaya Okislitel'naya Gazifikatsiya Benzina" (English version above) in Zhurnal Prikladnoy Khimii, Vol. 19, No. 7, Moscow, 1946, pages 632-650.

The process of the high-temperature decomposition of petroleum fractions for the purpose of obtaining gases rich in olefinic hydrocarbons has been the object of a number of studies (Bibl. 1, 2). Dubrovay, Chelintsev, et al (Bibl. 3), and subsequently Dobryanskiy and Bogomolov (Bibl. 4) discovered that the introduction of small amounts of oxygen into the process of thermal decomposition of hydrocarbons increases the total yield of the gas and the yield of the olefins -- ethylene, propylene, and butylenes.

Our goal was to investigate the process of obtaining gas from liquid fuel, as previously suggested by one of us (Bibl. 5, 11), considering that the forced method of obtaining rich hydrocarbon gases may find application in many branches of industry and national economy.

This method of gasification of hydrocarbons can be applied to obtain: (1) industrial gas; (2) rich power gas (for, among others, transport power installations); and (3) chemically valuable unsaturated gases.

The following postulate underlies the investigated process: (1) the

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† process of gasification should be completely autonomous in the thermal and chemical sense, which is of particular importance when this process is utilized ~~to obtain power gas~~. (2) this should be a high-temperature process, which is necessary to achieve a substantial gas yield and to "force" the process and the apparatus; and (3) the gasification should be oxidizing, because the volumetric determination ^{Introduction} of heat during oxidation is the most perfect and effective method of forcing heat into the zone of the endothermal decomposition reaction. The presence of oxygen should promote a more extensive dissociation of the original fuel, and the dilution of the fuel with nitrogen should retard the process of the formation of heavy molecules from the products of primary decomposition.

The thus developed process was termed by us "high-temperature oxidizing gasification" (Bibl. 5), which reflects most fully the specific features of this process. The difference between gasification and other processes, including pyrolysis and ^{Dubrovai's} oxidizing cracking, consists primarily in that the purpose of gasification, pre-determining the selection of all parameters of this process, is to obtain a maximal gas yield. The range of working temperatures, composition of the gasified mixtures, etc., all are geared to this purpose.

Selecting the Basic Parameters of the Process. A high unit productivity and high gas yield during the gasification can be achieved by applying high reaction temperatures. The optimal temperatu-

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†res may differ for different types of raw material, according to their fractional and group composition, because the speeds of ^{their} decomposition reaction may differ. An analysis of the available data (Bibl. 5) shows that these temperatures should be not below 800°C.

A rational construction of the thermal process, deep dissociation of the original fuel and minimal deposition of coke are achieved by using oxidizing decomposition, in which the dissociation proceeds in the presence of oxygen. In this case, the heat necessary to materialize the reaction is released uniformly throughout the mass and this eliminates a number of major technological difficulties involved in introducing a large amount of high-potential heat through the walls of the apparatus.*

The achievement of deep dissociation is most difficult when the yield of high-molecular products and carbon is low.

The specific effect of the dilution with air should both manifest itself primarily in the decrease in the partial pressure of the fuel and the products of its decomposition in the reaction zone. In general the decomposition reactions correspond well with the former, and the condensation reactions -- with the latter; thus, the decrease in the condensation of fuel because of dilution should reduce the speed of the condensation reactions without exerting an appreciable effect on the rate of decomposition.

*The technological advantages of the volumetric introduction of heat by means of oxidation have been investigated in sufficient detail by the originator of the method of oxidizing cracking, K. K. Dubrovay.

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† Only the nitrogen of the air can be considered as the inert diluent here. The chemical effect of the oxygen entering into the reaction is difficult to anticipate, because oxygen catalyzes both reactions. The catalytic influence of oxygen has been determined only

qualitatively, so far. Nonetheless, it appears quite right to postulate that oxidizing decomposition in the presence of comparatively high concentrations of oxygen should lead to a deeper dissociation of fuel than that brought about by a purely thermal decomposition.

The basic parameters determining the course of the process of oxidizing gasification are: temperature, reaction time, and air concentration. The study of the influence of these parameters on the character of the process, composition of the products, and thermal balance of the reaction is the purpose of the present investigation. The influence of other factors, such as pressure, size and design of the ^{reaction vessel} and wall material, was not investigated.

Approximate thermochemical and kinetic calculations and tentative experiments have led to the conclusion that in order to attain high gas yields and a low yield of high-molecular products of condensation, and to achieve thermal autonomy, the process should take place at temperatures of the order of 900-1,000°C, reaction time τ of the order of several hundredths of a second,

and air excess coefficients α^* of from 0.1 to 0.15. B-59 benzine was selected as the object of investigation. This selection was based on the following considerations. Preliminary experiments revealed that (as analogously indicated by Dubrovay (Bibl. 3)) the greater part of the liquid products of reaction boils out to the same extent as the starting fuel. In the case of benzine that part of products can be easily utilized for burning together with gas. The selection of ^{the} B-59 benzine was dictated by special circumstances. The optimal product would be the one containing the greatest amount of paraffinic hydrocarbons, because the the naphthenic and, especially, aromatic benzines are bound to yield a large amount of high-molecular products of condensations and tars.

Experimental Part

Working Method. The experiments were conducted in tubular reaction vessel 2 shown in Fig. 1, constituted by a tube of EYa-1-T steel measuring 25x20 mm in diameter and 1,100 mm in over-all length, and enclosed in heat insulation. The heating of the reaction vessel was effectuated by passing a low-voltage current through the tube's walls. The temperature of the vessel was adjusted (within the limits of $\pm 5^\circ\text{C}$) by means of a KGZKh heating controller manufactured by the "Pirometr" Plant with a sensor constituted by a chromel-alumel thermocouple. Fuel delivery was measured by means of fluid flowmeter 11 (Fig. 2). The flowmeter was provided with a set of

** See Page 5a

**Excess air coefficient" denotes the ratio of the amount of air in the mixture to the amount of air necessary for a complete combustion of the fuel present in the mixture. For a theoretically ideal mixture, $\alpha = 1$, while for a mixture with insufficient fuel $\alpha < 1$, and for a mixture with excess of fuel $\alpha > 1$.

calibrated nozzles whose graduation was periodically re-checked. During the experiments fuel delivery was maintained at a fixed rate. Fuel consumption was verified by weighing before and after the experiment.

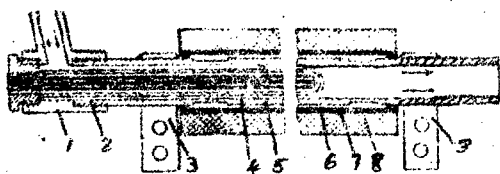


Fig. 1. Schematic Representation of the Reaction Vessel

1. T-pipe to supply mixture; 2. Reaction vessel;
3. Copper contacts; 4. Thermocouple casing;
5. Twin-duct porcelain midget tube; 6. Thermocouple;
7. Porcelain casing; 8. Heat insulation

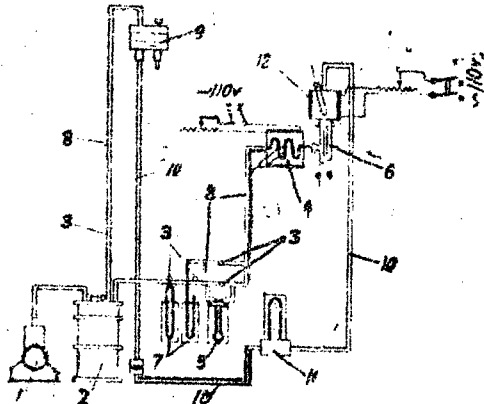


Fig. 2. Schematic Representation of the Supply of Fuel-Air Mixture to the Reaction Vessel

1. Pump; 2. Cushion; 3. Valve; 4. Preheater; 5. Rheometer;
6. Mixer; 7. Manometer; 8. Air feed; 9. Benzine tank;
10. Benzine feed; 11. Benzine meter; 12. Evaporator

The mixer is presented schematically in Fig. 3. The diaphragm on the outlet of the mixer was conducive to a rapid intermixing of fuel with air.

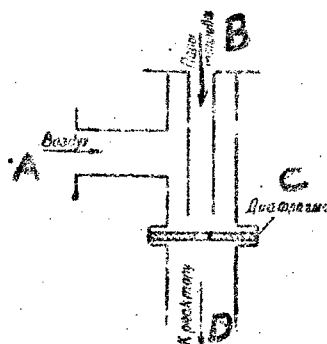


Fig. 3. Schematic Representation of Mixer

A - Air; B - Fuel vapors; C - Diaphragm; D - To reaction vessel

Fig. 4 shows the scheme of the cooling, measurement and collection of samples of the reaction products leaving the reaction vessel. The gases and vapors *Leaving* the reaction vessel through midjet tube 1 were cooled in two parallel metallic reflux condensers 2 and thereupon *bled off* through valve 3 or proceeded through valve 4 into the testing system. The condensate and water were driven off into flask 5 while the gas together with the fine-disperse mist of condensing fluid was fed into Smitt filter* 6 which drove off completely all the liquid phase, depositing it into flask 7.

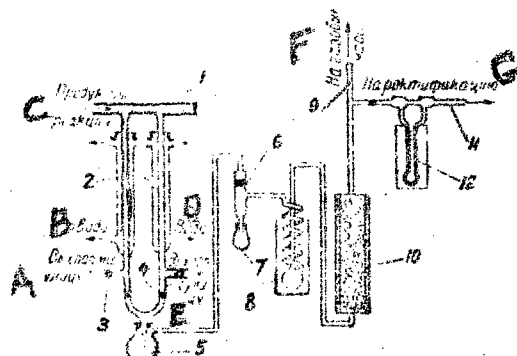


Fig. 4. Schematic Representation of the Measurement and Collection of Samples of Reaction Products

A - Bleed-off outlet; B - Water; C - Reaction products;
D - Water; E. Bleed-off outlet; F.-To gas meter;
G.- To rectification

*The Smitt filter consists of a compact parcel of glass wool and, when properly packed and sized, it prevents the passage of the minute fluid particles suspended in the gas.

Thence the gases and vapors proceed into large glass coil 8 immersed in a cooling mixture of ice and salt, where a part of the condensed water vapors and liquid hydrocarbons sedimented, and the remaining gases and vapors passed on through a silicagel-filled metering tube 10 and were bled off through valve 9 and the gas meter and burned out.

An average gas sample proceeded through valve 11 and the rheometer into the rectification column, which was cooled with liquid air. The uncondensed gases were collected in an emptied 20-liter tank. During the experiments the rate of delivery of gases into the system was maintained constant.

After heating the reaction vessel to the desired temperature, and after heating the preheater and evaporator to 350°C , the working mixture was blown through the apparatus for a few minutes and the reaction products were bled off (Fig. 4). Thereupon valve 3 was closed, ~~then~~ opening valve ^{4⁷} ^{opened} and the systematic recording of the instrument readings was commenced. The movement of the thermocouple along its casing was used to verify the temperature distribution along the reaction vessel. This was followed by conducting the rectification of the gas and driving off the products absorbed by the silicagel. After the cooling of the reaction vessel the thermocouple casing and the cap at the opposite end were unscrewed and the carbon on the walls of the reaction vessel was scraped off with a special brush. The obtained carbon was weighed.

and calcined in an air current at 120°C to a fixed weight. The difference in weight before and after the calcining was assumed to be the weight of the deposited carbon.

Reducing the

Material Balance Sheet. The theoretical amount of air needed for a complete combustion was accepted in all calculations at 15 kg per kg of benzine.

The material balance sheet of every experiment was drawn up by comparing the weight of the taken and the obtained substances. The amount of the obtained substance was determined in the following manner.

The amount of liquid hydrocarbon was determined by direct weighing.

The weight of the gas was determined as $\frac{\text{the mathematical}}{\text{product of its volume}}$ (on introducing corrections for temperature, pressure, moisture) and the volume-unit weight.

The amount of the forming water was computed according to the consumption of the introduced oxygen, on the assumption that the formation of water required an amount of oxygen equal to:

$$[\text{O}_2]_{\text{H}_2\text{O}} = [\text{O}_2] \left[\text{introduced} - [\text{O}_2]_{\text{CO}_2} - [\text{O}_2]_{\text{CO}} - [\text{O}_2] \right] \text{residue in gas}$$

The reason was because very little of the organic oxygen compounds were found in the reaction products, so that these compounds could not be taken into account when compiling the material balance sheet.

The yield of carbon was no higher than several tenths of a percent, and therefore it was not considered in the balance sheet.

The thus reduced material balance sheet involved deviations of normally not more than one or two percent. The experiments in which the deviations exceeded 3.5 percent were as a rule scrapped.

Analysis of Reaction Products

Analysis of Gas

Rectification of the gas was conducted in a device with a copper rectification column designed by the laboratory of the Khimgaz All-Union Scientific Research Institute of Chemical Treatment of Gases (Bibl. 7).

The content of olefins was determined by the sulfuric-acid method (Bibl. 12).

The content of CO_2 , CO, and C_2 was determined by the absorption method in an Ors type device.

The content of hydrogen was determined by burning over cupric oxide.

The content of saturated hydrocarbons was determined by burning over a platinum **coil**.

The weight of one liter of the gas was determined by the pycnometric method.

Analysis of Liquid Products

Specific gravity was determined by the pycnometric method.

Fractional composition was determined by Engler-type fractional distillation.

Mean molecular weight was determined by the cryoscopic method.

Content of actual tars was determined by the standard method of

evaporation in a bowl to a fixed weight. Inasmuch as the condensate contained a greater amount of tars compared with the benzines, therefore it was diluted by adding B-59 benzine.

The amount of the unsaturated reaction products in the fraction with b.p. of up to 200°C was determined by the method of bromine numbers.

The total content of unsaturated and aromatic hydrocarbons was determined by treatment with Kattwinkel's mixture.

It is the amount of actual tars in the products of gasification that constitutes an important index of the suitability of the gas for power installations. The values determined by the standard method cannot be considered accurate, because the degree of unsaturation of the liquid products of gasification is conducive to the formation of tars in the process of their determination. For instance, in the freshly driven off fraction with b.p. up to 150°C, in certain cases, as much as 75-100 mg of actual tars tended to form per 100 cm³ of the condensate in the course of the determination. Consequently, the tabulated tar yields could be regarded only as upper limits. The question of the possibility of using the obtained gas for power purposes without first purifying it from tars requires, therefore, a special study.

Processing the Results of the Experiments

Determining the "Reaction Temperature." Already the first few experiments had shown that the concept of reaction temperature is

purely nominal when applied to oxidizing gasification, because reaction is by its very nature non-isothermal.

During the evolution of a reaction the temperature field of the reaction vessel becomes strongly distorted, forming a peak at the beginning of the reaction zone, with the height of the peak depending on the composition of the mixture and the rate of its delivery. The determination of the mean temperature of such a reaction involves fundamental difficulties. Therefore, the nominal temperature, as adopted for processing the results of the experiments, was assumed to be the temperature at the end of the reaction zone, because, at given α and given contact time τ that temperature can serve to characterize the composition and properties of the gasified fuel. It should be added moreover that the temperatures measured by the thermocouple are not true temperatures of the gas, because of radiative heat exchange between the surface of the thermocouple's casing and the inner surface of the reaction vessel, and the presence of heat transfer along the wall of the thermocouple's casing, which causes the temperature distribution curve to become somewhat smoothed out.

Thus, "reaction temperature" according to which the results were classified, is nominal both inherently and in the sense of the method used to determine it.

Contact Time. Contact time was construed as the time of sojourn of the ^{original} benzene-air mixture in the reaction zone, with the unit volume

of that mixture being related to reaction temperature and to the pressure at the outlet of the air preheater. An increase in volume as a result of the reaction was not considered in the calculations because, on the one hand, this increase was relatively small in view of the considerable dilution of the air by nitrogen and, on the other, calculations according to the arithmetical mean of the unit volumes before and after the reaction do not, by any means, yield the true reaction time. Thus, the "true" reaction time is actually somewhat less than indicated in the tables -- on the average, about 1.2-1.3 times lower.

"Reaction Zone." Fig. 5 illustrates the method used to determine this zone. The length of the zone proved to be virtually identical in all experiments as a result of the comparatively high oxidation rate and the commensurate heating of the mixture to the starting sector of the zone.

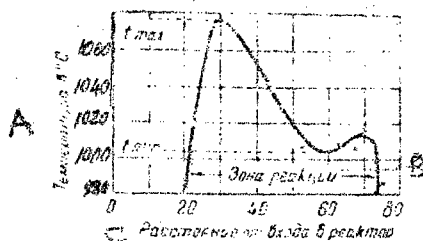


Fig. 5. Determining the Length of Reaction Zone

$\alpha = 0.15$; $\tau = 0.1$ second; $t = 1,000^{\circ}\text{C}$

A - Temperature in $^{\circ}\text{C}$; B - Reaction zone;

C - Distance from the inlet of the reaction vessel

Compiling the Tables. The tables were compiled by including only those experiments which had yielded a satisfactory coincidence between the material balance sheets and a satisfactory distribution of temperature in the reaction vessel. During the calculations of the yields by weight of the individual components, and during all the energy

calculations the losses of fuel in the experiments were proportionately divided among all the components. This is natural considering that the losses consisted not ^{so much} of actual losses of substance as of errors of individual measurements and analyses. The yield by weight of fluid is defined as the weight ratio of the combined liquid total amount of reaction products to the weight of the ^{original} benzine taken.

During the determination of the extent of transformation, the liquid hydrocarbons boiling out at up to 150°C which had not changed after treatment with Kattwinkel's mixture were regarded as untransformed fuel.

Inasmuch as the original fuel (B-59) contained approximately seven percent aromatic hydrocarbons, the magnitude determined in this manner is not an exact one; however, a more precise method of determining ^{the} "extent of transformation" could be hardly feasible in practice. The table of the composition by weight of the products of gasification (Table 3) serves as the starting table for all thermochemical calculations. The calorificity of the liquid products of reaction was determined by using an interpolation graph illustrating the relationship between calorificity and the specific gravity of the fluid. The maximum calorificity of the B-59 was assumed at 11,000 kilocalories/kg.

Results of the Experiments

Conditions of the Experiments and Systematization of Results. The experiments were conducted at temperatures of 810-830, 900 and 1,000°C for several different ^{values of α} and for a fixed $\tau = 0.1$ second. In addition, two series of experiments were conducted for variable τ at temperature of 1,000°C and at $\alpha = 0.13$ and $\alpha = 0.15$. The pressure in the reaction

vessel _____ varied from 1.25 to 1.4 atm during different experiments. The fluctuations in pressure during any single experiment did not exceed 0.1 atm.

The results of 20 experiments are cited in composite tables 1 and 2. Table 3 cites the distribution of the carbon and hydrogen of the original benzine among the individual reaction products. Figs. 7 to 23 illustrate the tabulated data and their recalculations in various forms. When examining the graphs of yield it should be taken into account that the curves they contain are not interpolative and indicate merely an approximate course of the variations in the yields of products under various conditions of experiments.

Table 1 - [See page 15a]

1. Composite Table of the Results of the Experiments;
2. No. of Experiment;
3. Conditions of Experiment;
4. Temperature, °C;
5. Extent of Transformation, in percent by Weight;
6. Yield of Fluid, in percent by Weight of Benzine
7. Yield of the Fractions Upward of 200°C, in percent by Weight of Benzine; with b.p. of
8. Yield of Tars, in percent by Weight of Benzine;
9. Characteristics of Liquid Products;
10. Boil. p. up to 200°C according to Engler;
11. Specific Gravity of Fluid;
12. Mean Molecular Weight;
13. Unsaturated, in percent;
14. Unsaturated + Aromatic, in percent;
15. Deviations from the Material Balance Sheet, in percent

ТАБЛИЦА I
Сводная таблица результатов опыта

№ опыта	Условия опыта		Глубина превращения в % по весу	Выход жидкости по весу от бензина	Выход фракции жидкости по весу от бензина	Выход смолы в % по весу от бензина	(2) Характеристика жидких продуктов				Расхождение на баланс в %		
	Температура °C	"					Вязкость до 20° С, по Бугару	Удельный вес жидкости	Средний молекулярный вес	Непрелетевшее в %		Непрелетевшее + паровая фракция в %	
42	830	0.03	0.1	71.2	45.4	2	0.22	95	0.762	101.5	12.1	29.0	+3.0
34	830	0.07	0.1	86.6	29.0	3.0	0.06	98	0.793	101.5	34.4	47	-
32	830	0.10	0.1	92.7	17.3	1.0	0.18	92	0.836	100.9	27.2	49	-3.0
43	830	0.15	0.1	93.5	13.4	1.05	0.104	94	0.834	91.2	10.1	47	-2
49	900	0.03	0.1	72.6	41.5	2.06	0.107	96	0.766	95.0	13.0	29	-7
48	900	0.07	0.1	84.7	29.2	1.98	0.227	94	0.792	100.6	15.0	41.0	-2
45	940	0.10	0.1	96.3	17.8	3.2	0.765	84	0.893	103.5	9.5	69.0	-
30	980	0.15	0.1	98.4	15.8	3.34	0.73	82	0.906	93.3	-	80.0	-0.4
39	1050	0.03	0.1	93.4	27.9	-	-	-	-	-	-	53.0	7.8
38	1000	0.07	0.1	95.2	21.5	7.2	2.2	-	-	102.5	16.7	70.0	-7
37	1050	0.10	0.1	94.7	14.6	1.7	0.25	92	0.841	90.3	16.3	57.0	-3.3
46	1000	0.13	0.1	96.7	15.4	3.7	0.68	80	-	95.0	13.9	47	-
47	1000	0.15	0.1	95.2	15.4	4.0	1.0	78	0.933	102.3	15.8	55	-
55	1000	0.13	0.025	98.2	24.6	0.94	0.06	96	0.781	-	-	20	-0.4
57	1000	0.13	0.037	94.2	14.1	1.01	0.163	91	0.838	-	-	49	-1.6
56	1000	0.13	0.05	99.4	9.9	0.67	0.082	94	0.876	-	-	69	-3.9
59	1000	0.13	0.075	96.7	14.7	8.8	0.52	74	0.919	-	-	66	-8.8
54	1000	0.15	0.019	89.2	18.4	1.23	0.038	97	0.792	-	-	28	+2.3
51	1000	0.15	0.03	93.4	12.5	1.33	0.104	92	0.839	98.3	13.3	25	-2.5
58	1000	0.13	0.05	96.9	9.6	1.17	0.138	92	0.857	-	-	60	-3.0

Table 2 *

1. Composite Table of the Results of the Experiments;
2. No. of Experiment;
3. Conditions of Experiment;
4. Temperature, °C;
5. Weight of one liter of Gas;
6. Composition of Gas;
7. Maximum Temperature in Reaction Vessel, °C

* See page 15a

ТАБЛИЦА 2
Сводная таблица результатов опытов

№ опыта	Условия опыта		Результаты	Состав газа										Максимальная температура в реакторе °C																																																																																																																																																																																																																																																																																																																																																																																																																																																																																							
	Давление, мм рт.ст.	Время, мин.		CO ₂	CO	O ₂	H ₂	CH ₄	C ₂ H ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂		C ₆ H ₆	C ₇ H ₈	C ₈ H ₁₀	C ₉ H ₁₂	C ₁₀ H ₁₄	C ₁₁ H ₁₆	C ₁₂ H ₁₈	C ₁₃ H ₂₀	C ₁₄ H ₂₂	C ₁₅ H ₂₄	C ₁₆ H ₂₆	C ₁₇ H ₂₈	C ₁₈ H ₃₀	C ₁₉ H ₃₂	C ₂₀ H ₃₄	C ₂₁ H ₃₆	C ₂₂ H ₃₈	C ₂₃ H ₄₀	C ₂₄ H ₄₂	C ₂₅ H ₄₄	C ₂₆ H ₄₆	C ₂₇ H ₄₈	C ₂₈ H ₅₀	C ₂₉ H ₅₂	C ₃₀ H ₅₄	C ₃₁ H ₅₆	C ₃₂ H ₅₈	C ₃₃ H ₆₀	C ₃₄ H ₆₂	C ₃₅ H ₆₄	C ₃₆ H ₆₆	C ₃₇ H ₆₈	C ₃₈ H ₇₀	C ₃₉ H ₇₂	C ₄₀ H ₇₄	C ₄₁ H ₇₆	C ₄₂ H ₇₈	C ₄₃ H ₈₀	C ₄₄ H ₈₂	C ₄₅ H ₈₄	C ₄₆ H ₈₆	C ₄₇ H ₈₈	C ₄₈ H ₉₀	C ₄₉ H ₉₂	C ₅₀ H ₉₄	C ₅₁ H ₉₆	C ₅₂ H ₉₈	C ₅₃ H ₁₀₀	C ₅₄ H ₁₀₂	C ₅₅ H ₁₀₄	C ₅₆ H ₁₀₆	C ₅₇ H ₁₀₈	C ₅₈ H ₁₁₀	C ₅₉ H ₁₁₂	C ₆₀ H ₁₁₄	C ₆₁ H ₁₁₆	C ₆₂ H ₁₁₈	C ₆₃ H ₁₂₀	C ₆₄ H ₁₂₂	C ₆₅ H ₁₂₄	C ₆₆ H ₁₂₆	C ₆₇ H ₁₂₈	C ₆₈ H ₁₃₀	C ₆₉ H ₁₃₂	C ₇₀ H ₁₃₄	C ₇₁ H ₁₃₆	C ₇₂ H ₁₃₈	C ₇₃ H ₁₄₀	C ₇₄ H ₁₄₂	C ₇₅ H ₁₄₄	C ₇₆ H ₁₄₆	C ₇₇ H ₁₄₈	C ₇₈ H ₁₅₀	C ₇₉ H ₁₅₂	C ₈₀ H ₁₅₄	C ₈₁ H ₁₅₆	C ₈₂ H ₁₅₈	C ₈₃ H ₁₆₀	C ₈₄ H ₁₆₂	C ₈₅ H ₁₆₄	C ₈₆ H ₁₆₆	C ₈₇ H ₁₆₈	C ₈₈ H ₁₇₀	C ₈₉ H ₁₇₂	C ₉₀ H ₁₇₄	C ₉₁ H ₁₇₆	C ₉₂ H ₁₇₈	C ₉₃ H ₁₈₀	C ₉₄ H ₁₈₂	C ₉₅ H ₁₈₄	C ₉₆ H ₁₈₆	C ₉₇ H ₁₈₈	C ₉₈ H ₁₉₀	C ₉₉ H ₁₉₂	C ₁₀₀ H ₁₉₄	C ₁₀₁ H ₁₉₆	C ₁₀₂ H ₁₉₈	C ₁₀₃ H ₂₀₀	C ₁₀₄ H ₂₀₂	C ₁₀₅ H ₂₀₄	C ₁₀₆ H ₂₀₆	C ₁₀₇ H ₂₀₈	C ₁₀₈ H ₂₁₀	C ₁₀₉ H ₂₁₂	C ₁₁₀ H ₂₁₄	C ₁₁₁ H ₂₁₆	C ₁₁₂ H ₂₁₈	C ₁₁₃ H ₂₂₀	C ₁₁₄ H ₂₂₂	C ₁₁₅ H ₂₂₄	C ₁₁₆ H ₂₂₆	C ₁₁₇ H ₂₂₈	C ₁₁₈ H ₂₃₀	C ₁₁₉ H ₂₃₂	C ₁₂₀ H ₂₃₄	C ₁₂₁ H ₂₃₆	C ₁₂₂ H ₂₃₈	C ₁₂₃ H ₂₄₀	C ₁₂₄ H ₂₄₂	C ₁₂₅ H ₂₄₄	C ₁₂₆ H ₂₄₆	C ₁₂₇ H ₂₄₈	C ₁₂₈ H ₂₅₀	C ₁₂₉ H ₂₅₂	C ₁₃₀ H ₂₅₄	C ₁₃₁ H ₂₅₆	C ₁₃₂ H ₂₅₈	C ₁₃₃ H ₂₆₀	C ₁₃₄ H ₂₆₂	C ₁₃₅ H ₂₆₄	C ₁₃₆ H ₂₆₆	C ₁₃₇ H ₂₆₈	C ₁₃₈ H ₂₇₀	C ₁₃₉ H ₂₇₂	C ₁₄₀ H ₂₇₄	C ₁₄₁ H ₂₇₆	C ₁₄₂ H ₂₇₈	C ₁₄₃ H ₂₈₀	C ₁₄₄ H ₂₈₂	C ₁₄₅ H ₂₈₄	C ₁₄₆ H ₂₈₆	C ₁₄₇ H ₂₈₈	C ₁₄₈ H ₂₉₀	C ₁₄₉ H ₂₉₂	C ₁₅₀ H ₂₉₄	C ₁₅₁ H ₂₉₆	C ₁₅₂ H ₂₉₈	C ₁₅₃ H ₃₀₀	C ₁₅₄ H ₃₀₂	C ₁₅₅ H ₃₀₄	C ₁₅₆ H ₃₀₆	C ₁₅₇ H ₃₀₈	C ₁₅₈ H ₃₁₀	C ₁₅₉ H ₃₁₂	C ₁₆₀ H ₃₁₄	C ₁₆₁ H ₃₁₆	C ₁₆₂ H ₃₁₈	C ₁₆₃ H ₃₂₀	C ₁₆₄ H ₃₂₂	C ₁₆₅ H ₃₂₄	C ₁₆₆ H ₃₂₆	C ₁₆₇ H ₃₂₈	C ₁₆₈ H ₃₃₀	C ₁₆₉ H ₃₃₂	C ₁₇₀ H ₃₃₄	C ₁₇₁ H ₃₃₆	C ₁₇₂ H ₃₃₈	C ₁₇₃ H ₃₄₀	C ₁₇₄ H ₃₄₂	C ₁₇₅ H ₃₄₄	C ₁₇₆ H ₃₄₆	C ₁₇₇ H ₃₄₈	C ₁₇₈ H ₃₅₀	C ₁₇₉ H ₃₅₂	C ₁₈₀ H ₃₅₄	C ₁₈₁ H ₃₅₆	C ₁₈₂ H ₃₅₈	C ₁₈₃ H ₃₆₀	C ₁₈₄ H ₃₆₂	C ₁₈₅ H ₃₆₄	C ₁₈₆ H ₃₆₆	C ₁₈₇ H ₃₆₈	C ₁₈₈ H ₃₇₀	C ₁₈₉ H ₃₇₂	C ₁₉₀ H ₃₇₄	C ₁₉₁ H ₃₇₆	C ₁₉₂ H ₃₇₈	C ₁₉₃ H ₃₈₀	C ₁₉₄ H ₃₈₂	C ₁₉₅ H ₃₈₄	C ₁₉₆ H ₃₈₆	C ₁₉₇ H ₃₈₈	C ₁₉₈ H ₃₉₀	C ₁₉₉ H ₃₉₂	C ₂₀₀ H ₃₉₄	C ₂₀₁ H ₃₉₆	C ₂₀₂ H ₃₉₈	C ₂₀₃ H ₄₀₀	C ₂₀₄ H ₄₀₂	C ₂₀₅ H ₄₀₄	C ₂₀₆ H ₄₀₆	C ₂₀₇ H ₄₀₈	C ₂₀₈ H ₄₁₀	C ₂₀₉ H ₄₁₂	C ₂₁₀ H ₄₁₄	C ₂₁₁ H ₄₁₆	C ₂₁₂ H ₄₁₈	C ₂₁₃ H ₄₂₀	C ₂₁₄ H ₄₂₂	C ₂₁₅ H ₄₂₄	C ₂₁₆ H ₄₂₆	C ₂₁₇ H ₄₂₈	C ₂₁₈ H ₄₃₀	C ₂₁₉ H ₄₃₂	C ₂₂₀ H ₄₃₄	C ₂₂₁ H ₄₃₆	C ₂₂₂ H ₄₃₈	C ₂₂₃ H ₄₄₀	C ₂₂₄ H ₄₄₂	C ₂₂₅ H ₄₄₄	C ₂₂₆ H ₄₄₆	C ₂₂₇ H ₄₄₈	C ₂₂₈ H ₄₅₀	C ₂₂₉ H ₄₅₂	C ₂₃₀ H ₄₅₄	C ₂₃₁ H ₄₅₆	C ₂₃₂ H ₄₅₈	C ₂₃₃ H ₄₆₀	C ₂₃₄ H ₄₆₂	C ₂₃₅ H ₄₆₄	C ₂₃₆ H ₄₆₆	C ₂₃₇ H ₄₆₈	C ₂₃₈ H ₄₇₀	C ₂₃₉ H ₄₇₂	C ₂₄₀ H ₄₇₄	C ₂₄₁ H ₄₇₆	C ₂₄₂ H ₄₇₈	C ₂₄₃ H ₄₈₀	C ₂₄₄ H ₄₈₂	C ₂₄₅ H ₄₈₄	C ₂₄₆ H ₄₈₆	C ₂₄₇ H ₄₈₈	C ₂₄₈ H ₄₉₀	C ₂₄₉ H ₄₉₂	C ₂₅₀ H ₄₉₄	C ₂₅₁ H ₄₉₆	C ₂₅₂ H ₄₉₈	C ₂₅₃ H ₅₀₀	C ₂₅₄ H ₅₀₂	C ₂₅₅ H ₅₀₄	C ₂₅₆ H ₅₀₆	C ₂₅₇ H ₅₀₈	C ₂₅₈ H ₅₁₀	C ₂₅₉ H ₅₁₂	C ₂₆₀ H ₅₁₄	C ₂₆₁ H ₅₁₆	C ₂₆₂ H ₅₁₈	C ₂₆₃ H ₅₂₀	C ₂₆₄ H ₅₂₂	C ₂₆₅ H ₅₂₄	C ₂₆₆ H ₅₂₆	C ₂₆₇ H ₅₂₈	C ₂₆₈ H ₅₃₀	C ₂₆₉ H ₅₃₂	C ₂₇₀ H ₅₃₄	C ₂₇₁ H ₅₃₆	C ₂₇₂ H ₅₃₈	C ₂₇₃ H ₅₄₀	C ₂₇₄ H ₅₄₂	C ₂₇₅ H ₅₄₄	C ₂₇₆ H ₅₄₆	C ₂₇₇ H ₅₄₈	C ₂₇₈ H ₅₅₀	C ₂₇₉ H ₅₅₂	C ₂₈₀ H ₅₅₄	C ₂₈₁ H ₅₅₆	C ₂₈₂ H ₅₅₈	C ₂₈₃ H ₅₆₀	C ₂₈₄ H ₅₆₂	C ₂₈₅ H ₅₆₄	C ₂₈₆ H ₅₆₆	C ₂₈₇ H ₅₆₈	C ₂₈₈ H ₅₇₀	C ₂₈₉ H ₅₇₂	C ₂₉₀ H ₅₇₄	C ₂₉₁ H ₅₇₆	C ₂₉₂ H ₅₇₈	C ₂₉₃ H ₅₈₀	C ₂₉₄ H ₅₈₂	C ₂₉₅ H ₅₈₄	C ₂₉₆ H ₅₈₆	C ₂₉₇ H ₅₈₈	C ₂₉₈ H ₅₉₀	C ₂₉₉ H ₅₉₂	C ₃₀₀ H ₅₉₄	C ₃₀₁ H ₅₉₆	C ₃₀₂ H ₅₉₈	C ₃₀₃ H ₆₀₀	C ₃₀₄ H ₆₀₂	C ₃₀₅ H ₆₀₄	C ₃₀₆ H ₆₀₆	C ₃₀₇ H ₆₀₈	C ₃₀₈ H ₆₁₀	C ₃₀₉ H ₆₁₂	C ₃₁₀ H ₆₁₄	C ₃₁₁ H ₆₁₆	C ₃₁₂ H ₆₁₈	C ₃₁₃ H ₆₂₀	C ₃₁₄ H ₆₂₂	C ₃₁₅ H ₆₂₄	C ₃₁₆ H ₆₂₆	C ₃₁₇ H ₆₂₈	C ₃₁₈ H ₆₃₀	C ₃₁₉ H ₆₃₂	C ₃₂₀ H ₆₃₄	C ₃₂₁ H ₆₃₆	C ₃₂₂ H ₆₃₈	C ₃₂₃ H ₆₄₀	C ₃₂₄ H ₆₄₂	C ₃₂₅ H ₆₄₄	C ₃₂₆ H ₆₄₆	C ₃₂₇ H ₆₄₈	C ₃₂₈ H ₆₅₀	C ₃₂₉ H ₆₅₂	C ₃₃₀ H ₆₅₄	C ₃₃₁ H ₆₅₆	C ₃₃₂ H ₆₅₈	C ₃₃₃ H ₆₆₀	C ₃₃₄ H ₆₆₂	C ₃₃₅ H ₆₆₄	C ₃₃₆ H ₆₆₆	C ₃₃₇ H ₆₆₈	C ₃₃₈ H ₆₇₀	C ₃₃₉ H ₆₇₂	C ₃₄₀ H ₆₇₄	C ₃₄₁ H ₆₇₆	C ₃₄₂ H ₆₇₈	C ₃₄₃ H ₆₈₀	C ₃₄₄ H ₆₈₂	C ₃₄₅ H ₆₈₄	C ₃₄₆ H ₆₈₆	C ₃₄₇ H ₆₈₈	C ₃₄₈ H ₆₉₀	C ₃₄₉ H ₆₉₂	C ₃₅₀ H ₆₉₄	C ₃₅₁ H ₆₉₆	C ₃₅₂ H ₆₉₈	C ₃₅₃ H ₇₀₀	C ₃₅₄ H ₇₀₂	C ₃₅₅ H ₇₀₄	C ₃₅₆ H ₇₀₆	C ₃₅₇ H ₇₀₈	C ₃₅₈ H ₇₁₀	C ₃₅₉ H ₇₁₂	C ₃₆₀ H ₇₁₄	C ₃₆₁ H ₇₁₆	C ₃₆₂ H ₇₁₈	C ₃₆₃ H ₇₂₀	C ₃₆₄ H ₇₂₂	C ₃₆₅ H ₇₂₄	C ₃₆₆ H ₇₂₆	C ₃₆₇ H ₇₂₈	C ₃₆₈ H ₇₃₀	C ₃₆₉ H ₇₃₂	C ₃₇₀ H ₇₃₄	C ₃₇₁ H ₇₃₆	C ₃₇₂ H ₇₃₈	C ₃₇₃ H ₇₄₀	C ₃₇₄ H ₇₄₂	C ₃₇₅ H ₇₄₄	C ₃₇₆ H ₇₄₆	C ₃₇₇ H ₇₄₈	C ₃₇₈ H ₇₅₀	C ₃₇₉ H ₇₅₂	C ₃₈₀ H ₇₅₄	C ₃₈₁ H ₇₅₆	C ₃₈₂ H ₇₅₈	C ₃₈₃ H ₇₆₀	C ₃₈₄ H ₇₆₂	C ₃₈₅ H ₇₆₄	C ₃₈₆ H ₇₆₆	C ₃₈₇ H ₇₆₈	C ₃₈₈ H ₇₇₀	C ₃₈₉ H ₇₇₂	C ₃₉₀ H ₇₇₄	C ₃₉₁ H ₇₇₆	C ₃₉₂ H ₇₇₈	C ₃₉₃ H ₇₈₀	C ₃₉₄ H ₇₈₂	C ₃₉₅ H ₇₈₄	C ₃₉₆ H ₇₈₆	C ₃₉₇ H ₇₈₈	C ₃₉₈ H ₇₉₀	C ₃₉₉ H ₇₉₂	C ₄₀₀ H ₇₉₄	C ₄₀₁ H ₇₉₆	C ₄₀₂ H ₇₉₈	C ₄₀₃ H ₈₀₀	C ₄₀₄ H ₈₀₂	C ₄₀₅ H ₈₀₄	C ₄₀₆ H ₈₀₆	C ₄₀₇ H ₈₀₈	C ₄₀₈ H ₈₁₀	C ₄₀₉ H ₈₁₂	C ₄₁₀ H ₈₁₄	C ₄₁₁ H ₈₁₆	C ₄₁₂ H ₈₁₈	C ₄₁₃ H ₈₂₀	C ₄₁₄ H ₈₂₂	C ₄₁₅ H ₈₂₄	C ₄₁₆ H ₈₂₆	C ₄₁₇ H ₈₂₈	C ₄₁₈ H ₈₃₀	C ₄₁₉ H ₈₃₂	C ₄₂₀ H ₈₃₄	C ₄₂₁ H ₈₃₆	C ₄₂₂ H ₈₃₈	C ₄₂₃ H ₈₄₀	C ₄₂₄ H ₈₄₂	C ₄₂₅ H ₈₄₄	C ₄₂₆ H ₈₄₆	C ₄₂₇ H ₈₄₈	C ₄₂₈ H ₈₅₀	C ₄₂₉ H ₈₅₂	C ₄₃₀ H ₈₅₄	C ₄₃₁ H ₈₅₆	C ₄₃₂ H ₈₅₈	C ₄₃₃ H ₈₆₀	C ₄₃₄ H ₈₆₂	C ₄₃₅ H ₈₆₄	C ₄₃₆ H ₈₆₆	C ₄₃₇ H ₈₆₈	C ₄₃₈ H ₈₇₀	C ₄₃₉ H ₈₇₂	C ₄₄₀ H ₈₇₄	C ₄₄₁ H ₈₇₆	C ₄₄₂ H ₈₇₈	C ₄₄₃ H ₈₈₀	C ₄₄₄ H ₈₈₂	C ₄₄₅ H ₈₈₄	C ₄₄₆ H ₈₈₆	C ₄₄₇ H ₈₈₈	C ₄₄₈ H ₈₉₀	C ₄₄₉ H ₈₉₂	C ₄₅₀ H ₈₉₄	C ₄₅₁ H ₈₉₆	C ₄₅₂ H ₈₉₈	C ₄₅₃ H ₉₀₀	C ₄₅₄ H ₉₀₂	C ₄₅₅ H ₉₀₄	C ₄₅₆ H ₉₀₆	C ₄₅₇ H ₉₀₈	C ₄₅₈ H ₉₁₀	C ₄₅₉ H ₉₁₂	C ₄₆₀ H ₉₁₄	C ₄₆₁ H ₉₁₆	C ₄₆₂ H ₉₁₈	C ₄₆₃ H ₉₂₀	C ₄₆₄ H ₉₂₂	C ₄₆₅ H ₉₂₄	C ₄₆₆ H ₉₂₆	C ₄₆₇ H ₉₂₈	C ₄₆₈ H ₉₃₀	C ₄₆₉ H ₉₃₂	C ₄₇₀ H ₉₃₄	C ₄₇₁ H ₉₃₆	C ₄₇₂ H ₉₃₈	C ₄₇₃ H ₉₄₀	C ₄₇₄ H ₉₄₂	C ₄₇₅ H ₉₄₄	C ₄₇₆ H ₉₄₆

Table 3 *

1. Distribution of Elements of Original Benzine Among the Products of Gasification, in percent by weight;
2. No. of Experiment;
3. Higher Unsaturated Compounds;
4. Oil;
5. Percentage /Ratio/ of C to the C of Benzine;
6. Percentage /Ratio/ of N to the N of Benzine;
7. Ratio of Column 15 to Column 12

*See page 17a.

ТАБЛИЦА 3
Распределение элементов исходного бензина между продуктами газификации, в % по весу

№ образца	распределение элементов исходного бензина между фракциями												Отношение граф. 15 к 12		
	CO ₂	CO	H ₂ O	H ₂	CH ₄	C ₂ H ₆	Всего непере- дельн.	Масло	% С к С бензина (5)			% Н к Н бензина (6)			
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
42	23	0,9	0,5	0,8	7,0	13,4	37,8	45,4	2,7	0,9	3,6	3,3	5,3	8,6	2,26
34	5,0	1,4	1,1	0,9	9,0	19,2	34,4	29,0	5,9	1,6	7,5	7,3	6,0	13,3	1,77
32	5,7	3,3	1,0	0,7	10,0	24,0	39,0	17,3	6,5	3,9	10,4	6,6	4,7	11,3	1,08
43	9,0	14,2	1,8	2,2	19,5	21,0	19,9	13,4	10,6	16,7	27,3	12,0	14,7	26,7	0,98
49	2,4	0,9	0,5	0,8	10,7	18,7	24,5	41,5	2,8	1,1	3,9	3,3	5,3	8,6	2,2
48	4,8	5,5	1,0	0,9	11,3	21,1	27,9	29,2	5,6	3,9	9,5	5,7	6,9	12,7	1,34
45	5,7	5,8	1,4	1,7	12,9	28,2	26,4	17,8	6,7	6,9	13,6	9,3	11,3	20,6	1,5
30	6,7	12,0	2,6	1,3	17,6	30,0	14,0	15,8	7,9	11,1	22,0	17,3	8,7	26,0	1,5
39	1,7	1,0	0,5	2,3	16,2	34,0	16,0	27,9	2,0	1,2	3,2	6,0	13,9	22,0	5,9
35	4,9	6,0	1,6	3,2	13,5	36,5	8,8	21,5	5,8	7,1	12,9	10,7	21,4	35,1	2,7
37	5,5	7,3	1,4	2,0	16,6	33,0	19,5	14,6	6,1	8,5	15,0	9,6	13,0	22,6	1,5
46	8,1	8,8	1,4	2,2	19,0	27,9	17,2	13,1	9,5	10,4	19,0	9,3	44,7	24,0	1,2
47	7,7	14,7	2,3	2,8	22,0	27,6	8,0	13,4	9,1	17,3	26,4	15,4	18,6	31,0	1,39
55	6,1	11,5	1,5	1,9	9,4	20,3	24,6	24,6	7,2	13,5	20,7	10,0	12,6	22,6	1,1
57	4,6	12,4	2,2	2,1	16,0	25,8	22,8	14,1	5,1	11,6	50,0	14,9	14,7	28,7	1,43
56	6,3	14,5	1,3	2,8	15,3	30,0	19,9	9,9	7,4	17,0	21,4	8,7	18,7	27,4	1,13
59	2,2	10,3	1,8	2,5	22,0	28,9	17,9	11,6	6,1	13,6	19,7	12,0	16,7	28,7	1,15
54	5,2	14,0	1,2	2,0	14,0	19,9	25,3	18,4	6,1	16,5	22,6	8,0	13,3	21,3	0,93
51	7,5	16,0	1,5	2,1	16,8	26,8	16,7	12,5	9,0	18,8	27,8	10,0	14,0	24,9	0,86
58	4,6	14,1	1,5	1,9	21,1	23,3	23,6	9,6	5,4	16,5	22,0	10,0	12,7	22,7	1,63

Temperature Regime. The curve of temperature distribution along the reaction vessel, shown in Fig. 5, is typical of an oxidizing-decomposition reaction involving a mixture with a substantial amount of oxygen. Under these conditions the effect of external heating manifests itself but little, because the greater the concentration of oxygen the smaller the amount of heat which has to be introduced into the reaction zone for the purpose of the thermal balancing of the process. When $\alpha = 0.13-0.15$, the introduction of external heat is in practice needed only to compensate the heat loss, and when $\alpha = 0.15$ and at a short contact time, the reaction proceeds nearly without any introduction of external heat.

The temperature field in these experiments should maximally reproduce the temperature field of an "adiabatic" reaction vessel. In the experiments with low values of α , when the fairly considerable consumption of heat on endothermal reaction is compensated by external heating, a sizable temperature drop existed between the external wall and the gas, which had distorted considerably the temperature field of the reaction and the results of measurements by the thermocouple.

All the curves of temperature distribution point to a high rate of oxidation and release of heat at the beginning section of the reaction vessel. In the experiments with low α the temperature remains approximately constant once it reaches its maximum. In the experiments with high α the temperature drops after it reaches its maximum (t_{\max} in Fig. 5), apparently because of the absorption of heat by the decomposi-

tion reaction, and it reaches its minimum (t_{\min} in Fig. 5), whereupon it again rises slowly, which we are inclined to ascribe to the condensation reactions of unsaturated products, accompanying the release of heat.

The degree of the non-isothermal state of the process could be characterized by the ratio $\Theta = \frac{t_{\min}}{\tau_{\max}}$, whose relationship to changes in temperature (when τ is constant) is illustrated in Fig. 6. As can be seen from Fig. 6, Θ decreases with increasing Θ_0 , which corresponds with the increasing autonomy of the process. The fact that the curve for 900°C extends below the curve for 830°C can be explained by the increase in extent of decomposition, accompanying the increase in temperature, and by the more extensive cooling of the reacting mixture. The progress of the curve for 100°C seems at first glance unexpected. The only plausible assumption would be that at higher temperatures the endothermal decomposition reaction reaches a comparatively high extent before the oxidation is yet completed, depressing the temperature peak, analogously to the fact that dissociation, increasing the so-called effective heat capacity, restricts the rise in the temperature of a high-temperature flame. The retardation in the rise in the maximal temperature of the process, commensurate with the increase in Θ_0 , and the decrease in the temperature difference ($t_{\max} - t_{\min} = \Delta T$) at a rise in reaction temperature, as illustrated in Fig. 7, could ^{both} be explained in the same manner.

Oxidation Stage. The schematic representation of oxidation and decomposition as independent and successive reactions reflects clearly the external thermal manifestations of the process. The chemistry of the process of oxidizing gasification is undoubtedly much more complex and the present study does not provide data for determining the chemical mechanism of the unfolding reactions.

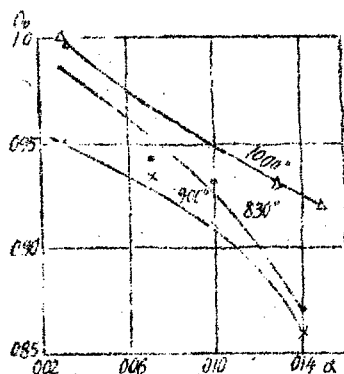


Fig. 6. Relationship Between the $\frac{t_{max}}{t_{max}}$ Ratio and α and t ($\tau = 0.10$ second)

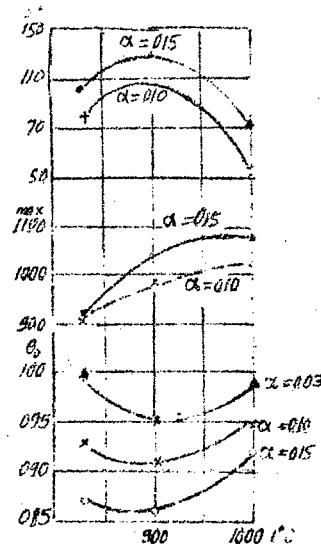


Fig. 7. Temperature Dependence of θ , t_{max} and Δt ($\tau = 0.10$ second)

The bound oxygen manifests itself in the gasification products nearly completely in the form of CO_2 , H_2O and CO . The percentile share of the oxygen that participates in the reaction proved to be virtually constant for the investigated values of τ (Fig. 8).

The presence in the gasification products, when T is low, of comparatively large amounts of fluid with a specific gravity of 0.78-0.79

(Fig. 10) and olefinic hydrocarbons (C_3 and C_4) (Fig. 14), indicates an incomplete decomposition. This makes it possible to state that the oxidation of the fuel, accompanied by a release of heat, ends long before the ending of the gasification. However, the question of how and through what intermediate stages does the process of oxidation proceed remains unclear; does there occur a primary association of oxygen, with the formation of aldehydes, alcohols, acids, and other acid-containing compounds, similarly to what occurs at lower temperatures, with a subsequent thermal decomposition of these substances; or does this process evolve in the form of a destructive oxidation with a deep disintegration of the fuel molecule during the elementary act itself of combination with oxygen, with direct formation of the final products of oxidation; or, lastly, do some intermediate stages take place?

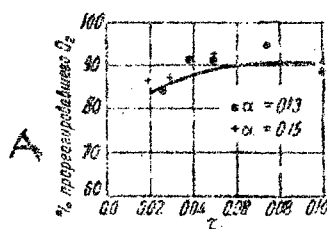


Fig. 8. Relationship Between Extent of Reacted Part of Oxygen and the Time of Contact

A - Percentage of reacted oxygen

Degree of Gasification.* Fig. 9 illustrates the yield by weight of the liquid hydrocarbons, serving to determine the degree of gasification. For all three temperatures the degree of gasification increases with increasing α which apparently is to be explained not only by the increase in the extent of dissociation as a result of the considerable amount of the oxygen participating in the reaction but, to a certain extent, also by the rise in the maximum temperature in the _____ reaction zone. However, the most _____ decisive factor is the high concentration of oxygen. This can be seen from the fact that the fluid yield when $\alpha = 0.03$ and $T = 1,000^{\circ}\text{C}$ is twice as high as the fluid yield when $\alpha = 0.15$ and $T = 830^{\circ}\text{C}$, although in the former case maximum temperature reaches $1,000^{\circ}\text{C}$, and in the latter -- only 920°C .

*The degree of gasification pertains to the relative (by wt. in percent) amount of the original liquid fuel that has become transformed into permanent gases (including C_4).

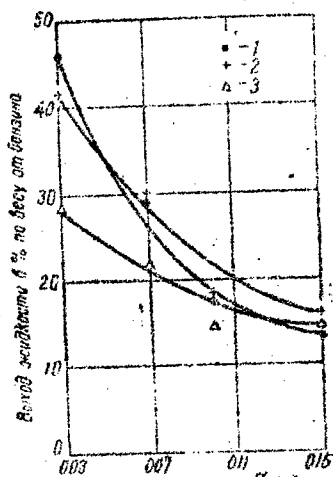


Fig. 9. Relationship Between Yield of Fluid By wgt. and α when $\tau = 0.1$ second
 * -- $t = 380^{\circ}\text{C}$; + -- $t = 900^{\circ}\text{C}$; Δ -- $t = 1,000^{\circ}\text{C}$.

A - Fluid yield in % by wgt. of benzine

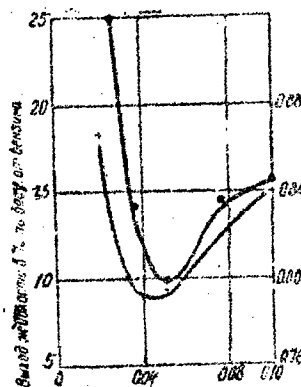


Fig. 10. Relationship Between Fluid Yield and Contact Time when $t = 1,000^{\circ}\text{C}$
 * -- $\alpha = 0.13$; + -- $\alpha = 1.15$
 A. Fluid yield in percent by weight of benzine

Fig. 10 illustrates the relationship between the yield of fluid (in percent by weight of the original benzine) and the reaction time at a temperature of 1,000°C, ^{and when} $\alpha = 0.13$, and $\alpha = 0.13$. It follows from these data that there exists a contact time at which the fluid yield is minimal. In measure with the increase in contact time the yield of fluid by weight gradually increases, and this is accompanied by a rise in the specific gravity of the fluid (Fig. 11).

The specific gravity of the fluid when τ is optimal, equals approximately the specific gravity of the aromatic hydrocarbons, and the amount of tars is very low.

The longer the reaction time the ^{more} rapid the rise in the specific gravity of the condensate and ⁱⁿ the yield of high-boiling-point fractions and tars, which indicates an intensive unfolding of secondary condensation reactions (Fig. 12).

See page 23a for Figs. 11 and 12.

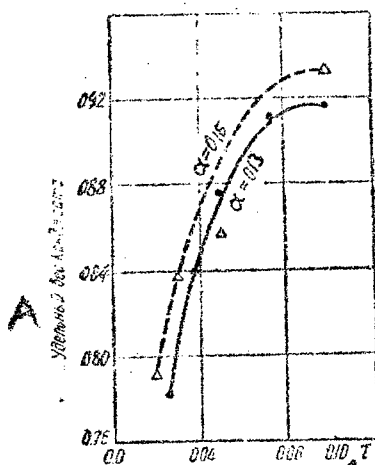


Fig. 11.

Relationship Between Specific Gravity of Condensate and Contact Time, $t = 1,000^{\circ}\text{C}$
 A - Specific gravity of condensate

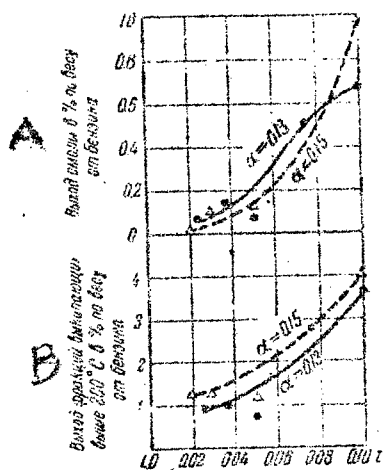


Fig. 12.

Relationship Between Yield of High-Boiling-Point Fractions of Condensate and Tar and Contact Time, $t = 1,000^{\circ}\text{C}$
 ● A - Yield of fractions boiling at upward of 200°C in percent by weight of benzene
 B - Yield of tar in percent by weight of benzene

Yield of Unsaturated Gases and the Mean Degree of Unsaturation of the Hydrocarbon Products of Gasification. The changes in the yield of unsaturated gases according to the conditions of experiments are of special interest. The yield of C_3-C_4 -olefins decreases quickly (when T is identical) with rising temperature. The yield curves for each of the investigated temperatures have a maximum along α . An explicitly expressed maximum along α is also displayed by the curves of the total yield of unsaturated gases.

The yield of ethylene increases steadily, and the yield of unsaturated C_3-C_4 s decreases with rising temperature (Fig. 13). The optimal α is identical for all temperatures and equals 0.1.

The afore-cited data [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100] pertaining to a single value of contact time are not exhaustive enough to determine the achievable optimal yields of unsaturated reaction products. The optimal conditions for obtaining unsaturated gases could be established only by comparing the yields of these gases under values of α various λ and contact times, optimal for all temperatures.

The mean degree of unsaturation of the hydrocarbon products of the decomposition reaction could be characterized by the ratio of the amount of carbon to hydrogen as associated in these products, which ratio we will hereinafter denote by S for brevity.

For a given initial magnitude of this ratio in the original raw material (S_0) the magnitude of S in the normal pyrolysis is determined by the amounts of free hydrogen and solid carbon released

in the course of the reaction. On expressing the amount of carbon by the number of C-atoms, and the amount of hydrogen by an half of the number of H-atoms in a hydrocarbon molecule, we find that $S_o = 1$ for all monoclefins and saturated naphthenes without side chains, $S_o = 2$ for benzene, and $S_o = \frac{2n}{m}$ for the C_nH_m hydrocarbon in the general form (Fig. 14).

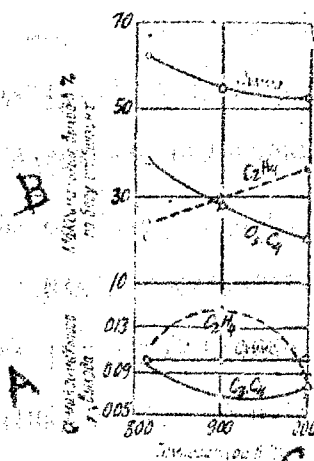


Fig. 13. Conditions of Maximal Yield of Unsaturated Gases, $\tau = 0.1$ seconds.
A - τ of maximal yield;
B - Maximal yield in percent by weight of benzene

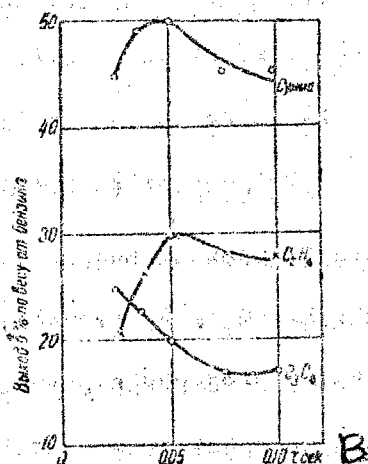


Fig. 14. Relationship Between Yield of Unsaturated Gases and S_o When $\tau = 0.13$ and $t = 1,000^\circ C$.
A - Yield in percent by weight of benzene;
B - τ seconds

If it is considered that $S_o = 0.95$ even in such a paraffinic benzene as the investigated B-59, it becomes clear that the obtainment of large amounts of a gas consisting of monoclefins, lower paraffins and hydrogen necessarily involves substantial yields of high-molecular condensed compounds including even coke.

The introduction of oxygen into the thermal decomposition reaction may in principle alter significantly the above-outlined picture, because the mutual association of a part of hydrocarbon and hydrogen into CO_2 , CO and H_2O is bound to reflect itself in the mean degree of unsaturation of the hydrocarbon products of decomposition. Here the effect of the introduction of oxygen should hinge on both the relative amount of oxygen and its distribution among the oxidation products. It is therefore natural that the clarification of the laws governing the distribution of oxygen among the oxidation products acquires special importance.

The lower part of Fig. 15 illustrates the relationship between the ^{ratio of} share of the carbon of the original fuel that has become oxidized into CO and CO_2 to the share of the hydrogen oxidized in water and the ^{value of} α . As can be seen from Fig. 15, this ratio was greater than unity throughout the investigated range of temperatures in all experiments save one, and undoubtedly it increases with an increasing α .

Thus, if no specific effect of oxygen on the formation of free hydrogen is presupposed, the introduction of air should foster a decrease in the mean degree of unsaturation of the hydrocarbon products of decomposition. The influence of temperature on this ratio is apparently not great and it is clearly overshadowed by the fairly wide spread of experimental points. The upper part of the same Fig. 15 illustrates the ratio (let us denote it by γ) of the

share of the oxygen-bound carbon to the share of hydrogen in water and in free state. This ratio also grows with an increasing α for all temperatures, reaching unity when $\alpha = 0.15$. Under these conditions ($\gamma = 1$) the degree of unsaturation of the hydrocarbon products of the reaction is $\delta = \delta_0$, which could never have been achieved during a non-oxidizing decomposition. The effect of temperature is difficult to determine in this case also, the more so as the comparison of data pertaining to an identical contact time is arbitrary in nature. In effect, when temperature rises but τ remains constant, the yield of hydrogen increases not only because of a more extensive decomposition but also because of the ^{greater} extensiveness of the secondary condensation reactions unfolding with the release of free hydrogen. The increase in the yield of free hydrogen and in the cited degree of unsaturation of the hydrocarbon reaction products (δ/δ_0) with increasing contact time, as shown in Fig. 16, corroborate the above. Equal conditions for comparing the results obtained at different temperatures would be constituted by a comparison of the measurements conducted at an identical -- in the physical sense -- contact time, e. g., at a contact time corresponding to a minimal yield of fluid.

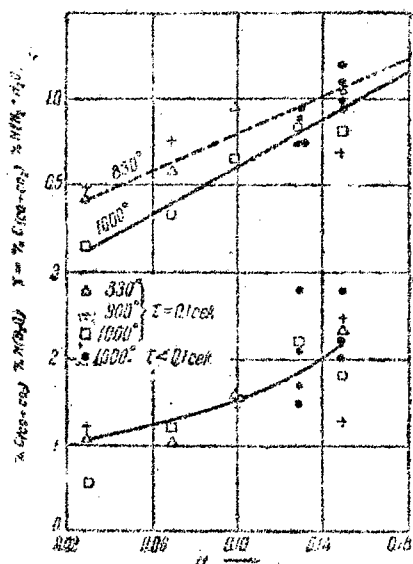


Fig. 15. Influence of the Concentration of Air on the Composition of the Non-Hydrocarbon Products of Gasification.

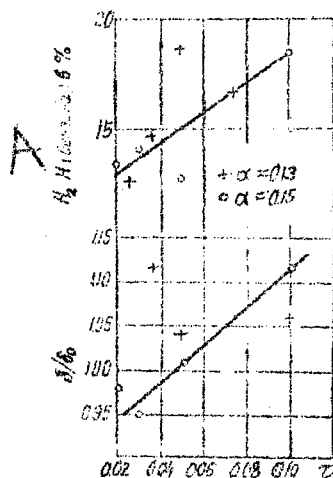


Fig. 16. Relationship Between Yield of Free Hydrogen and Degree of Unsaturation of the Hydrocarbon Products of Reaction and the Strictness of the Regime
A - H_2/H (benzine) in %

The character of the change in γ does not in itself reflect the change in δ which, as can be easily demonstrated, equals

$$\delta/\delta_0 = \frac{1-h}{1-h} = 1 + \frac{h}{1-h} (1-\gamma)$$

where h denotes the share of hydrogen that went on the formation of water and of the hydrogen present in free state in the reaction products.

It follows from the above equation that the afore-cited degree of

unsaturation decreases with increasing γ . As for the increase in the magnitude of h , this increases S when $S < 1$ and decreases S when $S > 1$. It can be seen from Fig. 17 that the magnitude of h increases with increasing α approximately like γ , and it is this that results in the feeble dependence of S on α up to $\alpha \approx 0.13-0.15$, (as illustrated in Fig. 18) which is the starting point for the decrease in S (the asterisk in Fig. 19 pertains to the data of an experiment conducted when $\alpha = 0.20$, $T = 900^\circ\text{C}$, and $\tau = 0.10$ second).

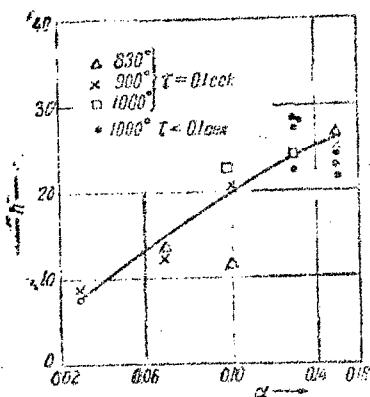


Fig. 17.

Relationship Between h and α

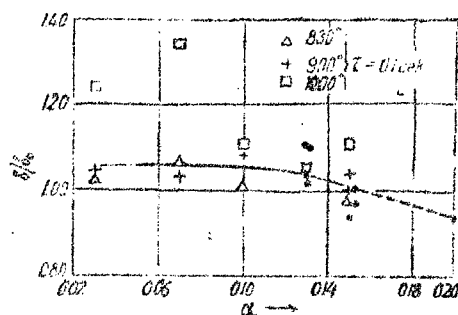


Fig. 18.

Relationship Between the Mean Degree of Unsaturation of Gasification Products and α
 * -- 1,000°C; $\tau < 0.1$ second.

Thus, the optimal gasification to obtain power gas would be that conducted when $\alpha \geq 0.15$ and at ^a short contact time. An excessive increase in α , leading to a decrease in the total yield of hydrocarbon reaction products, would not promote the obtainment of technological gas.

It should be noted that the foregoing statements pertain to a definite range of temperatures within which the dissociation reaches a considerable extent, i. e., it pertains to gasification. At the

temperatures used for *

{ Dubrovay-type oxidizing

cracking the laws might be different, not only because of the possible differences in the distribution of ~~the~~ oxygen among CO , CO_2 and H_2O and the smaller extent of dissociation but also because at temperatures of $500-600^\circ\text{C}$ the amount of the higher products of oxidation still remains comparatively large.

Fig. 19 shows the relationship between changes in mutual the ratio of the amounts of carbon and benzine oxidized in CO_2 and CO , respectively, and changes in α and temperature. As can be seen from Fig. 19, CO_2 predominates in the oxidation products when α is low, and CO , when α is high. The rise in temperature at a low α leads to an increase in the relative yield of CO , whereas when α is high (≈ 0.15) the effect of temperature is hardly appreciable.

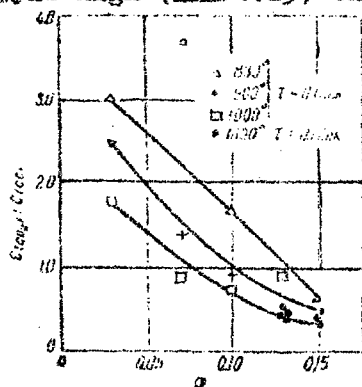


Fig. 19. Relationship Between Ratio of Carbon Content in CO_2 to Carbon Content in CO and the α .

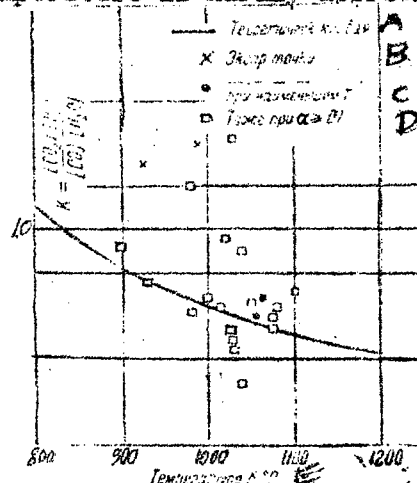


Fig. 20. The Problem of Determining the Equilibrium of Water Gas During Gasification.

- A - Theoretical curve;
- B - Experimental point;
- C - When T is minimal
- D - Also when $\alpha \geq 0.1$
- E - Temperature in $^\circ\text{C}$

The vital importance of the manner of the distribution of oxygen to the nature of the reaction products makes it particularly important to clarify the laws governing this process and the possibilities for controlling them. In Fig. 20 the points denote for all 20 experiments the values of the ratio

$$\frac{[\text{CO}_2] \cdot [\text{H}_2]^2}{[\text{CO}] \cdot [\text{H}_2\text{O}]} = K$$

against maximal temperature in reaction zone. The solid-line curve represents the change in the equilibrium constant of water gas according to temperature, after Gan (Bibl. 10). The experiments for $\alpha \gg 0.1$ are denoted by small squares. Two experiments at 1,000°C, $\alpha = 0.13$ and $\alpha = 0.15$ and the minimum τ (0.025 and 0.02, respectively) are denoted by circles. As can be seen from Fig. 20, the points lie closely along the curve when $\alpha \gg 0.1$ and when the temperatures range approximately from 1,000 to 1,050°C, which makes it possible to assume that at such values of α and temperatures the relative concentrations of H_2O , H_2 , CO_2 , and CO are determined by the conditions of the equilibrium of the water gas.

Of extreme interest is the question whether it is possible, through a preliminary introduction of water-gas constituents into the reaction zone, to alter substantially the distribution of the oxygen of the air among the products of deep oxidation and thus to influence the mean degree of unsaturation and the composition of the hydrocarbon products of gasification. Even if the added water will not, because of its

great chemical strength, participate in the reaction, the presence of this excess water in the reaction zone would be bound to lead to the formation of relatively large amounts of carbon oxides and thereby also to a decrease in δ , if only the equilibrium of the water gas would materialize itself. A converse effect can be expected when CO_2 is introduced in advance into the reaction zone.

Distribution and Balance of Heat-Producing Capacity in the Gasification Products. For an efficient construction of the gasification process it is essential to be familiar with the total thermal balance of the process. The data in Table 3 make it possible to compute the total heat-producing capacity of products and, on comparing it with the heat-producing capacity of the original benzine, to determine the heat loss during the gasification process. Fig. 21 illustrates the loss of the heat-producing capacity (in percent) of the original benzine in the course of its gasification as according to contact time, at a temperature of $1,000^\circ\text{C}$, in two mixtures with a different composition ($\alpha = 0.13$ and $\alpha = 0.15$). The course of the curves shown coincides satisfactorily with the interpretation of the process of oxidizing gasification provided in Sections 2 and 3.

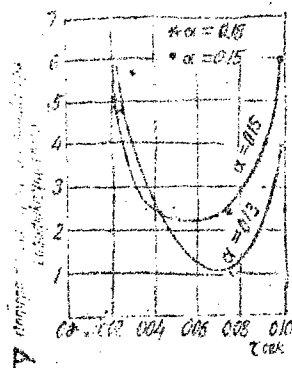


Fig. 21. Relationship Between the Loss in the Heat-Producing Capacity of the Original Fuel During Gasification and the A- loss in the heat-producing capacity of the fuel during gasification (in percent)

During the first stage of the process, during oxidation and incipient decomposition of the gasified fuel, the decrease in the chemical energy of the fuel results in the release of heat which heats up the mixture to a high temperature, in which connection the heat-producing capacity of the fuel declines. The subsequent deep endothermal dissociation results in the absorption of the heat and its re-conversion into the chemical energy of the fuel. As the contact time increases in duration the secondary exothermal condensation reactions reduce again the useful heat-producing capacity of the gasified fuel. Thus, minimal loss takes place at a contact time during which the process of the primary dissociation of the fuel comes to an end and the secondary \square condensation reactions do not yet attain a considerable extent. A comparison of Fig. 21 with Fig. 10 shows that the minimal loss of heat-producing capacity and the minimal yield of fluid take place at approximately equal contact time, which

confirms the above-exposed scheme of the process.

To determine the change in the loss of heat-producing capacity at changes in α and in temperature, it would be necessary to compare this loss for the values of contact time corresponding to the minimum of the curves of "loss of heat-producing capacity--contact time." However, we possess such data only in relation to two gasification regimes, and therefore data obtained at an identical contact time of $\tau = 0.1$ second were plotted in Fig. 22 for the entire range of the investigated values of α . The blackened-in circles denote the loss at optimal values of T for $\alpha = 0.13$ and 0.15 . As can be seen from Fig. 22, the heat-producing capacity of gasification products decreases with increasing α and increases with rising temperature. When $\alpha = 0.03$, for all three temperatures, the heat-producing capacity of the reaction products is greater than the heat-producing capacity of the original fuel, whence it follows that under these conditions the over-all reaction proceeds by absorbing the heat introduced by electric heating. With increasing α the consumption of heat on the dissociation of the fuel becomes increasingly supplied by the release of heat from the oxidization of the fuel, until, at a certain value of α , both these values [of heat] level out one another. Any further increase in α will then already lead to a loss of the heat-producing capacity of the fuel. A rise in temperature leads to an increase in the extent of the decomposition of the fuel, and therefore the thermal balancing of the process

requires the introduction of an appropriately large amount of oxygen. The curves in Fig. 22 make it possible to evaluate the order of magnitude of the heat of dissociation of the fuel during gasification, and its temperature-dependence. Fig. 23 illustrates the relationship between the heat of dissociation, computed per kg of benzine, and temperature. The circles denote the data of the calculation for a variable α , and the crosses, for $\alpha = 0.15$. During the calculations it was assumed that 90 percent of the mixture's oxygen enters into the reaction (Fig. 8), and it was considered that, in accordance with the distribution of O_2 at every point, a part of the oxygen oxidizes carbon to CO and not to CO_2 . We ignored the difference in the heat content of the mixture before and after the reaction.

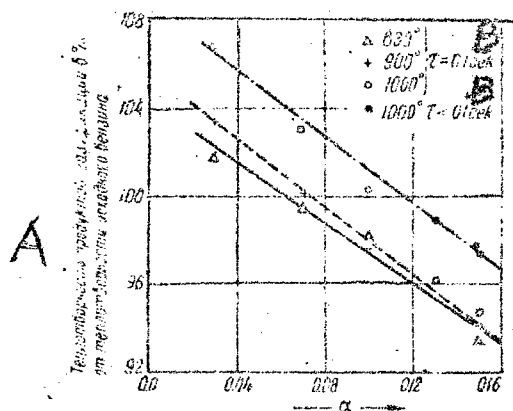


Fig. 22.

Relationship Between Heat-Producing Capacity of Gasified Fuel and α and T.

A - Heat-producing capacity of gasification products in percent of the heat-producing capacity of the original benzene.

B - Sec.

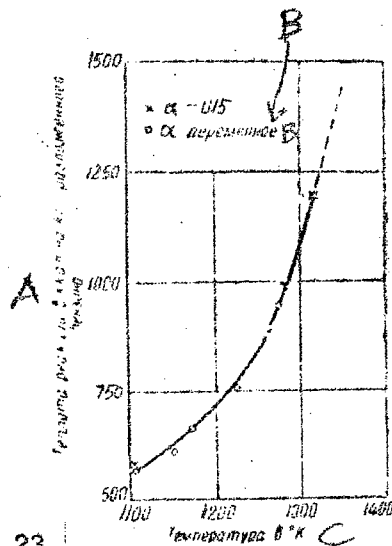


Fig. 23.

Relationship Between the Heat of Dissociation and Temperature. X - $\alpha = 0.15$;

O - α corresponding to the thermal balancing of the process.

A - Heat of reaction in kilocalories per kg of dissociated benzene;

B - Variable α

C - Temperature in $^{\circ}\text{K}$ [sic]

Regarding the course of the curve, it is pertinent to note the following: the investigated temperature range is distinguished by being precisely the one within which certain products of thermal dissociation of hydrocarbons, stable at lower temperatures, begin to decompose themselves, which leads to an increase in the extent and hence also heat of the dissociation. This pertains particularly to methane which is virtually totally stable at temperatures of up to 800°C , and to ethane and ethylene which decompose at a still comparatively slow rate at temperatures lower than 800°C . With decreasing temperature the reaction passes over to a range within which the above-enumerated decomposition products (and farther on, also others -- propane, propylene, etc.) become final products so that as a consequence the heat absorbed by the reaction decreases -- naturally, -- until it becomes equal to zero at the temperature of the beginning of dissociation ($\sim 400^{\circ}\text{C}$).

Conclusions

The study of the oxidizing gasification of B-59 benzine has

revealed the following:

(1) Under identical temperature and time conditions the introduction of oxygen into the process increases considerably the extent of dissociation of the fuel.

(2) The entire process could be described as a three-stage one. First occurs a rapid exothermal reaction of destructive oxidation, and then an endothermal decomposition reaction, which in turn is

followed by the condensation of the unsaturated decomposition products. According to conditions (mainly temperature), these successive stages may more or less overlap.

(3) The decomposition reaction and the secondary condensation reactions are clearly separated in time, so that through an appropriate selection of the time of contact it is possible to attain an extremely high degree of gasification (up to ~90 percent) with a low yield of condensation products.

(4) Every temperature has its own optimal values of α and contact time resulting in the maximal yield of _____: unsaturated gases. The largest obtained yield of unsaturated gases amounted to 62 percent by weight of the benzine. The largest -- 36 percent -- yield of ethylene was obtained at 1,000°C.

(5) The distribution of oxygen among the final products of oxidation together with the yield of free oxygen determines the mean degree of unsaturation of the hydrocarbon products of gasification and by the same token the _____ useability of the gas in power installations and as technological gas. The mean degree of unsaturation of the hydrocarbon products of reaction does not change until $\alpha = 0.13$ and 0.15, whereupon it begins to decrease rapidly.

(6) A comparison of the _____ above-obtained data with the isochore of the reaction of water gas provides a foundation for assuming that when $\alpha \geq 0.1$ and at maximal 1,000-1,050°C temperatures in the reaction zone, the composition of the non-hydrocarbon products is regulated by the equilibrium of the water gas.

In this connection, it is of utmost interest to make a special study of the possibility of regulating the process by an arbitrary shift of the equilibrium through the addition of various specific non-hydrocarbon products of reaction to the original mixture.

Bibliography

1. Tropsh. "Ind. Eng. Chem.," 30, 169 (1938)
2. Pich ler. "Brennst. Chem.," 16, 404 (1935)
- 3.
1. Tropsh. "Ind. Eng. Chem.," 30, 169 (1938) -- Pich ler. "Brennst. Chem.," 16, 404 (1935)
2. French Patents 119035, 154000, 192101. American Patents 1995136, 1823593. British Patents 448470, 440432, 468729, and others.
3. Dubrovsk and Sheinman. "Oxidizing Cracking," ONTI (1936)
4. Dohryanskii and Bogomoïov. "Works of the 'Khimgaz' Plant." Leningrad (1936)
5. Rivin. "Gasification of Heavy Liquid Fuel," unpublished MS (1938), Library of the Institute of Chemical Physics, Academy of Sciences USSR
6. Freg and Hepp. "Ind. Eng. Chem.," 24, 282 (1923)
7. Moor and Shilyayeva. "Works of the 'Khimgaz' Plant," 2 (1935)
8. Evans. "Trans. Far. Soc.," 35, 824 (1939)
9. Dol'kh. "Water Gas," ONTI (1938), page 30
10. "Z. anorg. Chem.," 35, 5 (1904)
11. Author's Application TN 18191
12. "Methods of Technical Analysis Applicable to the Synthesis of Hydrocarbon Fuels," Gostoptekhnizdat (1941)

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